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SILVER OR GOLD? SURPRISING CHALLENGES IN CLEANING A 19TH-CENTURY PERSIAN WATER PIPE

ARIEL O'CONNOR, MEG CRAFT, GLENN GATES, AND JULIE LAUFFENBURGER

A heavily tarnished 19th-century Persian water pipe, or *nargile*, made of gilded silver decorated with gemstones required cleaning for exhibition at the Walters Art Museum. X-ray fluorescence spectrographic analysis indicated an alloy of silver with copper, gold, and lead. Standard methods for mechanical tarnish reduction were tested, but all produced a silver-colored surface. Further x-ray fluorescence spectrographic analysis revealed that even the gentlest mechanical method—solvent cleaning with a cosmetic sponge—removed gold from the surface. Chemical test cleaning with acidified thiourea, or "silver dip," removed tarnish and preserved gold, but research has shown problems with this method, including potential leaching of copper, microetching, residual surface complexes, and increased light reactivity. Pros and cons of each method were considered, and thiourea was selected as least harmful. Methods for the safe use of thiourea in this context are discussed, and a new approach with non-woven cotton pads is introduced for cleaning.

KEYWORDS: Silver, Silver Cleaning, Gilding, Erasers, Thiourea, Silver Dip, Cleaning, Polishing

1. BACKGROUND

During the summer of 1903, Walters Art Museum founders William and Henry Walters traveled to Constantinople and purchased a group of 13 elaborately decorated objects made of precious metals and stones. Among these objects was a spectacular *nargile* (WAM 49.2199), or Persian tobacco water pipe, commonly called a *hookah*, stylistically dated to the mid-19th century (fig. 1).

Since 1934, when the nargile was bequeathed to the Walters Art Museum, no museum records were created, and it is unlikely the object has been cleaned or studied at the museum. The object was brought to the conservation lab in 2014 in preparation for exhibition. The conservation goal was established jointly with the curatorial department and included stabilization, surface cleaning, and materials and technology identification that could help inform treatment and elucidate the manufacture of this complicated object.

This article will only focus on the cleaning and tarnish reduction of the metal alloy components on the object, as the other components received standard conservation treatments.

2. MATERIALS, CONSTRUCTION, AND CONDITION

The nargile is an elaborately constructed and striking object that stands more than two feet tall and is composed of silver alloy, Chinese porcelain, and Persian enamel, and studded with rubies, emeralds, and turquoise.

The nargile was in stable condition but significantly altered by layers of tarnish. Interpretation of the object was difficult due to the variability of the appearance of the component metal parts. The repoussé metal components on the nargile not covered in tarnish were golden in appearance, but the smooth undecorated metal areas without tarnish had a silvery tone. The object is constructed from the sections shown in figure 2.

The lower third of the object functions as the water jar and unscrews from the top so that water can be added. The water jar is made from the bottom of a Chinese blue and white porcelain vessel, possibly from the 1720s.[1] The ceramic is set into a tarnished silver alloy metal mount with eight vertical ribs, each pinned at the top and soldered at the base.

Fig. 1. Overall view of the nargile before treatment. Artist unknown, *Nargile*, mid-19th century, ceramic vessel ca. 1720, gilded silver and copper alloy, porcelain, enamels, rubies (spinels), emeralds (beryls), dimensions with lid: 66.5 × 17.5 × 16 cm. The Walters Art Museum, 49.2199 (Courtesy of the Walters Art Museum)

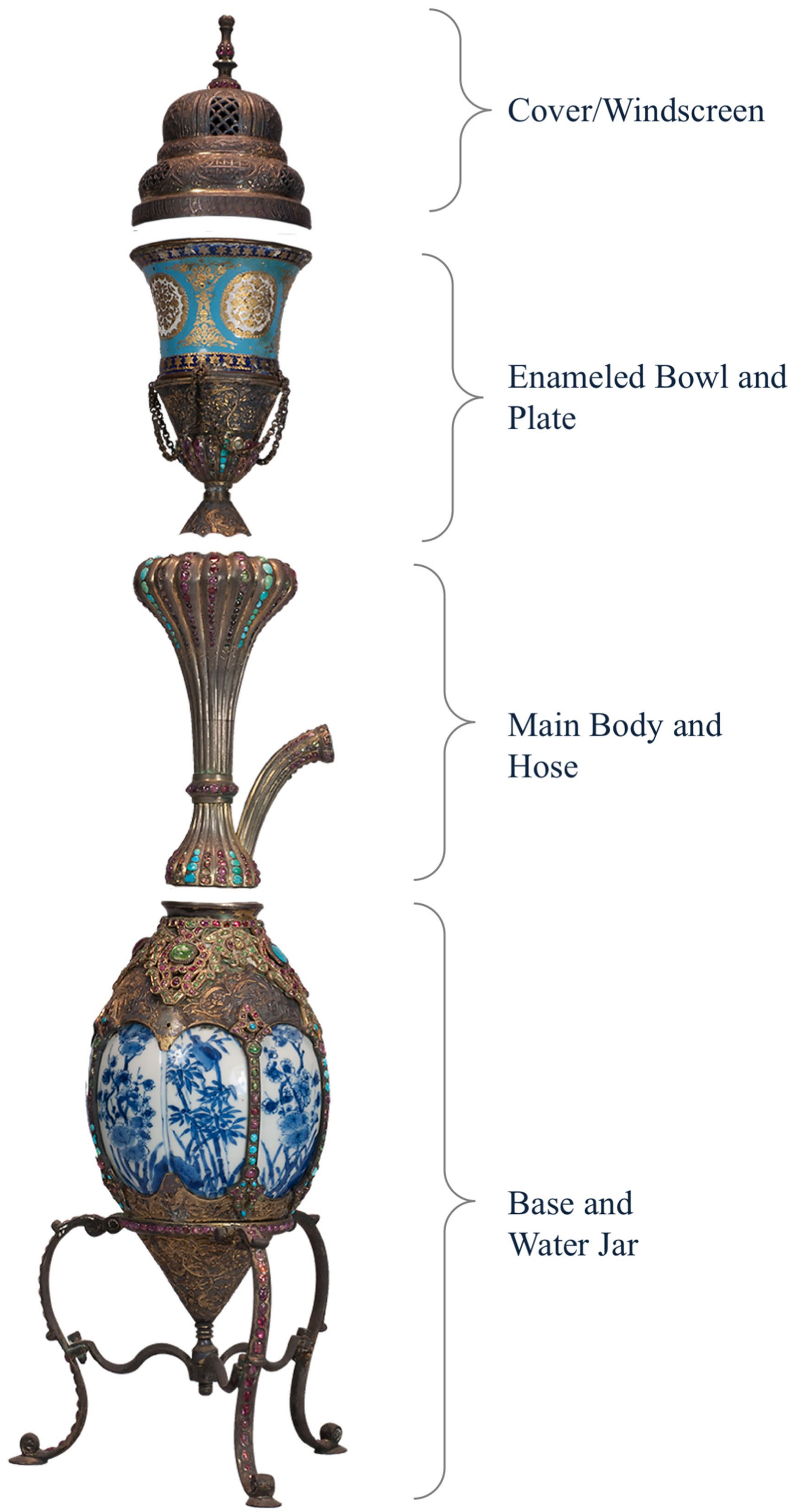

Fig. 2. Diagram of the nargile's primary sections (Courtesy of the Walters Art Museum)

Fig. 3. Detail of metal mount before treatment, highlighting engraved and stamped designs (Courtesy of the Walters Art Museum)

The tarnished metal mount is ornamented with repoussé and engraved floral designs (fig. 3), and the metal ribs are set with rows of cabochon gemstones (fig. 4). The bottom of the mount terminates in a cone-shaped point and is screwed into a cast tripod base with an equally tarnished surface. The tripod base is composed of five parts attached with modern screws. The metal and porcelain are held together with a black resin-like adhesive and cannot be separated.

Sitting directly above the water jar, the main body is a smooth silver-colored metal alloy with vertical fluted ridges. Two vertical halves were constructed by hammering, and vertical solder seams join the two sections. The smooth undecorated metal surface of this section stands in contrast to the elaborately textured patterns of the nargile's other metal components. This section is more "silvery" in tone and color than the rest of the object. The ridges are set with rows of cabochon rubies, emeralds, and turquoise. The hose is missing.

Above the body sits an inverted metal cone with a repoussé floral design, which acts as a decorative support for a fluted metal cup inlayed with cabochon gemstones and a scalloped upper ridge. This fluted cup sits at the base of a Persian-style enameled bowl. Inside, a perforated metal plate originally held the tobacco.

The cover, which sits at the top of the nargile, functions as a windscreen to prevent wind from increasing the burn rate and temperature of the coal. This very thin cover is made from a silver alloy base

Fig. 4. Varied gemstones pictured from all surfaces. A missing ruby reveals the silvered sheet and red dye underneath, indicated with a white arrow (Courtesy of the Walters Art Museum)

metal, hammered and raised from a single sheet of metal. Small air holes were punched or cut from the outside, inward. The surface was decorated with repoussé and chasing. A modern screw is soldered upside down on the top. A decorative finial sits loosely over the screw and is turned from a solid piece of metal and decorated with cabochon rubies and emeralds.

The gemstones used to decorate the surfaces are cabochon rubies, emeralds, and turquoise (fig. 4). The rubies and emeralds vary in color and clarity. To set the stones, individually cut holes were made in the metal specific to the outline of each stone. Each stone is backed with a tiny square piece of thin metal foil (fig. 4). Visual evidence suggests that this sheet is a copper alloy with a silvered surface. The silver-colored side of the sheet reflects light. To homogenize the unevenly colored stones, a colored dye in a gum-like medium was applied to the metal foil.

3. XRF ANALYSIS[2]

Prior to cleaning, analysis of the metal surface with XRF was undertaken to help characterize the complex metal components because of extreme variation in the object's current appearance. We hoped to understand the original coloration of the surface under the black tarnish, as some areas appeared silver and others gold. An understanding of the materials would help inform the methods selected for the cleaning tests.

The XRF survey of the metal components indicated a silver alloy with an enriched or gold-plated surface in most areas, with individual parts of the nargile having slightly different constituents and alloying ratios.

Although absolute quantification was not possible, a rough estimation of the alloy used for the water jar was obtained by comparison to silver metal standards; this indicated an alloy of approximately 85% to 90% silver, with approximately 5% copper, 5% gold, and 1% lead. No zinc or mercury were detected. The height of the low energy M-line peak for gold, relative to the standards, provided an indication that there was gold at the surface (fig. 5). No mercury was detected, so we did not have an amalgam gilding layer. XRF also identified strong sulfur peaks in the black tarnished areas. The finial and middle have the same silver, copper, gold, and lead elements, but in slightly different proportions than the water jar. The lid and tripod base both contain zinc, and very little gold was detected.

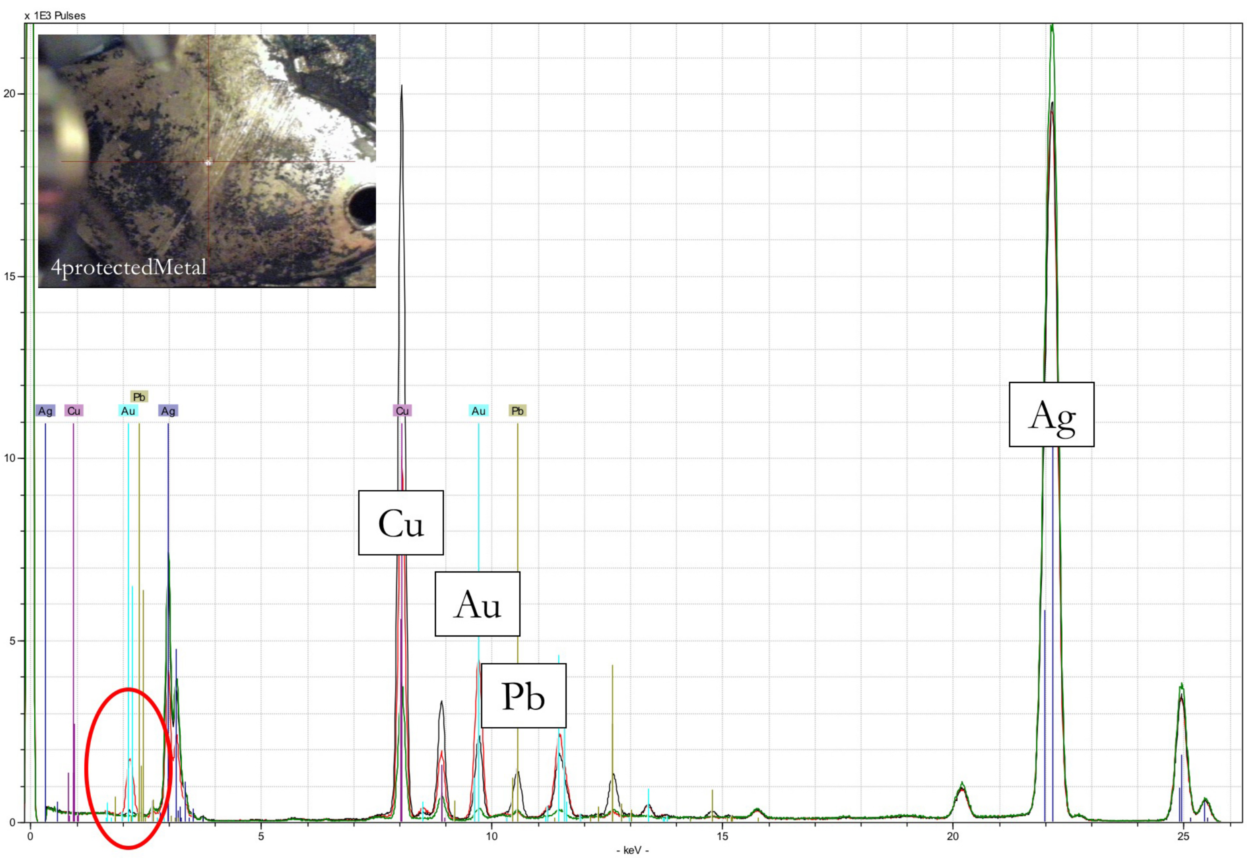

Fig. 5. XRF spectrum before cleaning of metal surface in a protected and untarnished area under a rib in section B. XRF shows the surface of the object to be mostly silver, with a small amount of copper, gold, and lead. This spectrum is overlaid with two standard samples for a rough estimation of ratio. The red circle highlights the M-line peak for gold (Courtesy of the Walters Art Museum)

All alloys display extensive silver sulfide corrosion with a variable surface appearance. Although questions still remained as to the original intention of the metals' appearances and whether or not there was a gilding layer, we decided to move forward with cleaning tests. It was our hope that these tests, combined with XRF information, could uncover the original surface treatment and intention.

4. MECHANICAL CLEANING TESTS

Following surface analysis, small cleaning tests were performed on each section of the nargile. While selecting a cleaning methodology, two problems posed the largest concern: rinsing the intricately textured metal surfaces and the dye under the gemstones.

The textured surface of the metal could easily trap traditional polish materials and chemical cleaning solutions, making rinsing and clearing difficult. In addition, the fragile gemstones were backed with a dye and gel-like medium that are highly soluble in most solvents, especially ethanol.

Because of these concerns, initial cleaning focused on mechanical silver-cleaning methods that would leave minimal to no residue. These methods included solvents on cotton swabs, cosmetic sponges, calcium carbonate, commercial polishes, and vinyl erasers. The cleaning tests were evaluated visually and deemed effective if they reduced the tarnish, worked effectively in tight spaces, and left a minimal residue (table 1).

Table 1. Mechanical Cleaning Tests

Material	Notes	Effective?
Stoddard's solvent, cosmetic sponge	Picked up dark tarnish on sponge, but no visible change in thickest tarnish areas.	No
Stoddard's solvent, cotton swab	Picked up light tarnish on swab, and some visual change on the object, but no visible difference in thick tarnish areas.	No
Goddard's Long Shine Silver Cloth	Picked up tarnish, but difficult to use in tight, small spaces.	No
Precipitated $CaCO_3$ in distilled H_2O, cotton swab	Effective, but slow. Left an unacceptable residue that was difficult to remove from textured surface.	No
Duraglit commercial silver polish, cotton swab	Aluminum oxide abrasive. Very effective at removing thick tarnish; no loose residue to remove. Good option for flat metal areas without gemstones. Clearing required.	Yes
Staedtler Mars plastic erasers (no. 526-52)	Most effective of all options tried with regard to both speed and ease of use. Erasers could be cut to size and rubbed on the tarnished areas, quickly removing tarnish. When dipped in water or mineral spirits, this process was faster than other methods.	Yes

Fig. 6. Cleaning window on base with Staedtler Mars plastic erasers dipped in deionized water. Note the silvery tone of the cleaned area compared to the untarnished golden-toned highlights on the adjacent uncleaned area (Courtesy of the Walters Art Museum)

Despite the compositional differences revealed earlier with XRF and indications of a gold enriched surface, all mechanical cleaning methods and materials consistently revealed a bright silver surface underneath. Erasers were selected as the most efficient method of cleaning, as they did not leave a residue on the textured surface and were safe to use around the perimeter of the stones without affecting the dye or swelling the carrier material. The erasers would be used dry around gemstones. On areas of metal without gemstones, the erasers would be dipped in distilled water or mineral spirits.

After the initial cleaning tests, a 1 × 1 in. cleaning window was opened on the base with Staedtler Mars erasers (fig. 6). The erasers removed the silver sulfide tarnish from the surface evenly, did not leave a residue, and could be used safely around the gemstones. Similar to the small tests mentioned earlier, this cleaning window had a silvery tone.

Given that XRF indicated the possibility of a gilding layer at the surface, we were surprised to see how silvery the surface appeared after cleaning compared to the small untarnished areas elsewhere that had a golden tone. Surprisingly, all methods of mechanical cleaning, even soft cosmetic sponges, yielded a bright silver surface. This visual discrepancy initiated discussions: was the original gold surface extensively worn from use or pre-1934 restoration so the surface now appeared silvery, or was our cleaning technique damaging the surviving gold surface?

5. CHEMICAL CLEANING TESTS

To understand the connection between mechanical cleaning and the silver appearance, we explored a chemical cleaning method. In the past, the Walters conservation lab used "silver dip," a traditional silver cleaning method using acidified thiourea. This methodology works as the acidic component dissolves the tarnish layer and the thiourea complexes the silver ions, allowing both to be rinsed away with water. However, this practice had fallen out of favor in recent decades, as research uncovered that thiourea could remove gold, complex with copper and trace minerals, and etch the microstructure of the silver surface (Barger et al. 1982; Selwyn 1990; Contreras-Vargas et al. 2013; van Santen 2014).

The traditional recipe in the Walters lab files used 5 ml sulfuric acid, 8 g thiourea, and 100 ml distilled water. We also tested solutions made with citric acid, but these were too slow and required multiple applications.

A comparative test was done on the metal rib detached from section A in an area with thick black sulfide corrosion (fig. 7). Silver dip was applied with a cotton swab, rolled on a 1 cm^2 area for 10 seconds, then cleared with deionized water on a cotton swab rolled gently across the surface. Two passes were sufficient to remove the sulfide and reveal a golden tone underneath. This gold-colored test area is seen on the far right side of figure 9, highlighted in yellow.

A second cleaning test was conducted in an adjacent area with similar sulfide corrosion. This area was cleaned mechanically using the softest of the mechanical methods tested—a cosmetic sponge with mineral spirits. The sponge picked up tarnish but could not remove all of the sulfide corrosion. The metal revealed through the tarnish had a silvery tone. This test spot is seen at the far left side of figure 6, highlighted in white.

Finally, a third cleaning test was done in the middle, first with silver dip to remove the sulfide, followed by half of the area cleaned with a cosmetic sponge and mineral spirits. The silver dip pass removed the sulfide corrosion and left a golden surface. After a few light passes with the sponge on half of the test area, the surface color changed from gold to silver.

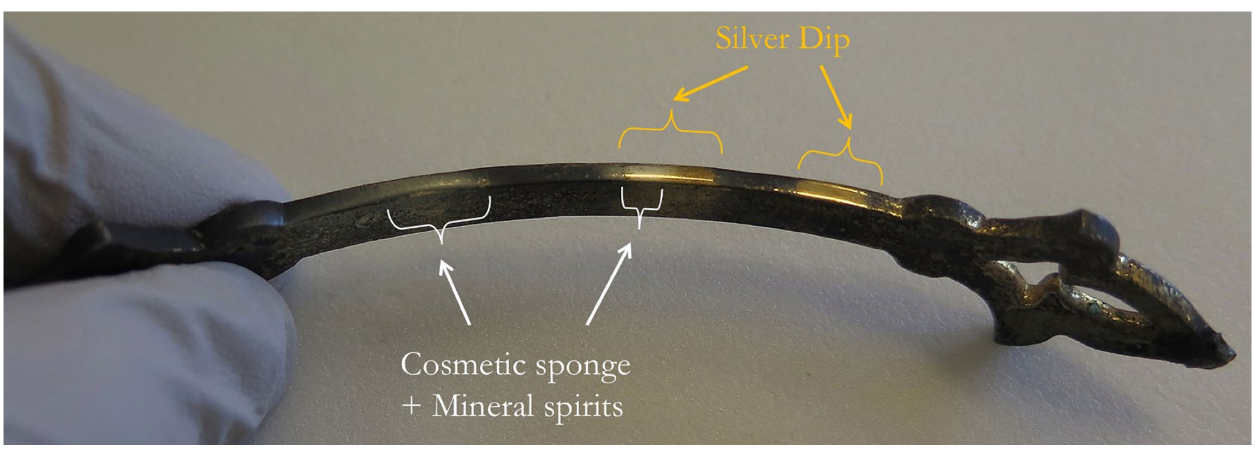

Fig. 7. Comparative mechanical and chemical cleaning tests on detached rib edge with thick sulfide corrosion. Note the silver tone of the cosmetic sponge areas and the golden tone of the silver dip areas (Courtesy of the Walters Art Museum)

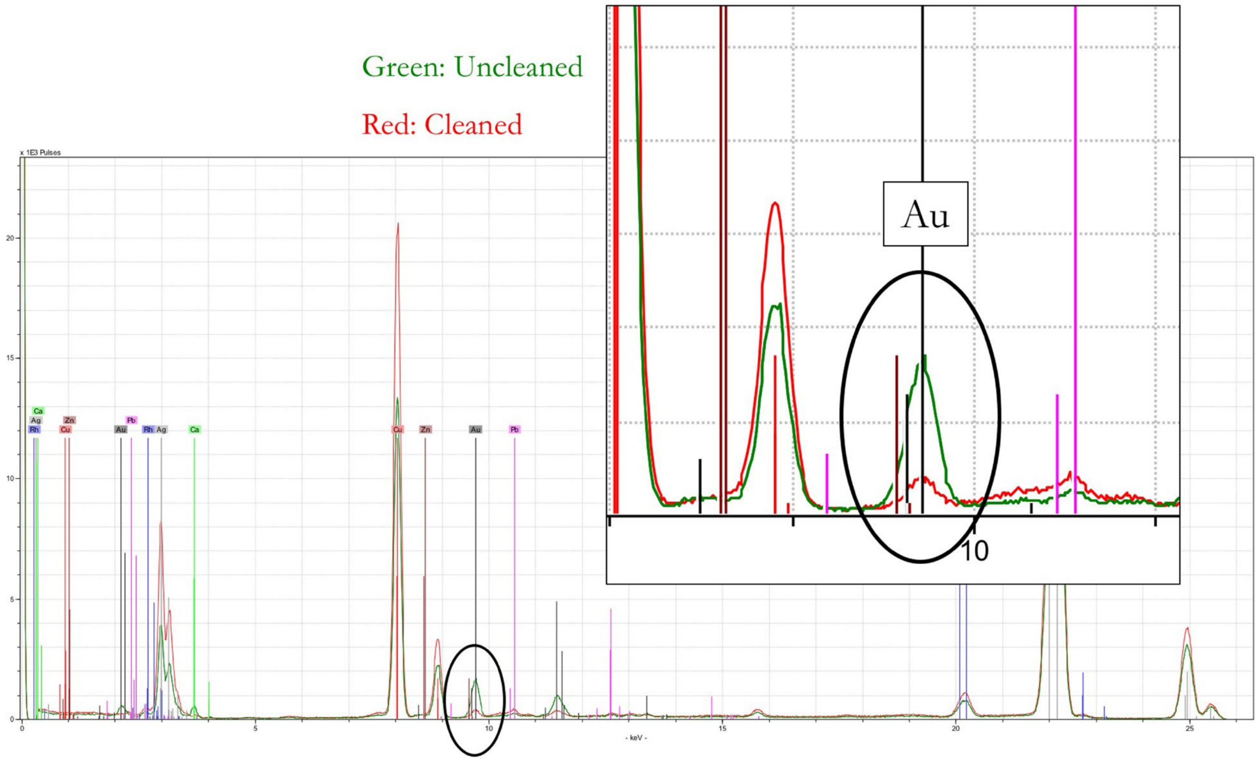

Fig. 8. XRF spectra of the cleaning tests on the rib before and after cleaning with a cosmetic sponge. The uncleaned surface shows a strong gold peak, whereas the cleaned surface shows much less surviving gold (Courtesy of the Walters Art Museum)

XRF was used to compare the mechanical and chemical cleaning methods. The area cleaned with a cosmetic sponge and mineral spirits showed a significant reduction in gold and a visual change to silver (fig. 8). We were surprised to discover that the soft cosmetic sponges were abrasive enough to remove the incredibly thin gilding layer. XRF of the dirty eraser crumbs from the earlier mechanical cleaning tests revealed that they contained gold.

6. DECISION

Conservation was left with a difficult decision between a mechanical cleaning that reduced surface gilding and a chemical cleaning with unknown aging properties in proximity to solvent-soluble dyes. An ideal conservation approach might postpone treatment until a later date when another cleaning method might be determined. However, the exhibition schedule required treatment to be completed quickly. The final decision was an informed compromise.

Other cleaning options, such as electrolytic cleaning, gels, or lasers, required further lengthy testing and research.

7. TREATMENT

Silver dip seemed to be the safest option for the artifact in our current situation. To ensure that we were using thiourea in the safest practical manner, we consulted with other conservators who had surveyed the literature (Pouliot and Nichols 2015) and have extensive practical experience using silver dip (Meighan and Lins 2015). After consultation, we believed that the silver dip could be used safely on this object by following the proper precautions, which are listed as follows. The silver dip should be left on the surface for less than 60 seconds—the amount of time it is safe before the solution could potentially attack different phases of the metal alloy (Meighan and Lins 2015). Since we could not immerse this object in any type of alkaline wash afterward because of the gemstones, it was stressed that we needed to rinse the area very well with distilled water (Meighan and Lins 2015). During cleaning, no swabs should be double-dipped into the silver dip, as this risks redepositing metal ions from the corrosion onto the object's surface. For the health and safety of the conservator and lab, the work must be carried out in a fume hood, as hydrogen sulfide gas is produced during the cleaning. With these precautions and steps in place, the treatment moved forward using silver dip as the sulfide cleaning methodology.

The goal of this treatment approach was an efficient and minimally abrasive reduction of the black sulfide tarnish layer. A simple cotton poultice application was developed that would keep the silver dip in contact with the surface without unnecessary abrasion (fig. 9). A large area could be covered with less abrasion using cotton Webril Handi-Pads cut to the size of the desired cleaning area. A 1 in. × 1 in. pad ended up being an optimal size for most areas, but it varied as the surface texture and shape changed.

Once the cotton pad was in place on the object, a plastic dropper was used to add silver dip to the surface until saturated but not dripping. This was left in place for approximately 20 seconds; a gloved finger was used to gently press the wet cotton against the surface. This proved useful in minimizing applications on textured areas.

The cotton pad was removed and thrown away, and the area was wiped thoroughly and immediately with a new cotton pad pre-dipped in distilled water. If needed, the process was repeated until the tarnish was removed. Most areas required only two passes. By using the cotton pads, abrasion to the fragile gilded surface was kept to a minimum.

The biggest challenge was cleaning the metal surface in areas adjacent to stones, which covered the majority of the artifact's surface. In these areas, the silver dip was added to the cotton before applying to the surface to prevent excess liquid near the stones. Thin cotton strips were cut for the rib sides adjacent to gemstones. If a particular area was too dry when applied, more silver dip could be added carefully with the dropper. If a cotton pad could not fit in recesses or undercuts, swabs were used gently.

After tarnish reduction, it was decided not to apply a coating, as the surface cannot withstand the abrasion needed to remove the coating in the future. Passive methods must be used to prevent retarnishing. The exhibition case was fitted with Pacific Silvercloth covering the air intake openings to filter the air before it reached the case. For storage, the object is wrapped with tissue, then silver cloth, and stored in a sealed polyethylene bag.

Fig. 9. Before, during, and after a thiourea application on the base with a pre-cut Webril cotton pad (Courtesy of the Walters Art Museum)

7.1 SILVER-TONED ERASER TEST CLEANING AREA

The eraser-cleaned test area had a silver tone and was brighter than the gold tone of the adjacent areas cleaned with silver dip. Several ideas were discussed to inpaint this aesthetic discrepancy, including a toned lacquer coating, thin acrylic wash, or even a new gold displacement application. In a case study where silver coins were cleaned with thiourea, a slight gold-colored tone was observed on the silver after cleaning (Contreras-Vargas et al. 2013). This phenomenon is due to hydrogen sulfide gas produced during cleaning, which can induce the formation of sulfides on the surface, giving a slight golden tone (Contreras-Vargas et al. 2013).

The slight color shift was not perceptible on the nargile's thiourea-cleaned areas with surviving gilding, but a test on the eraser-cleaned area of our object confirmed that the silver looked more golden after thiourea treatment. Ultimately, it was decided to re-clean this test area with the silver dip. The golden tone was achieved, and the entire object was treated with the same solution and methodology. The surfaces will age in a similar manner without an application of selectively placed coatings.

Fig. 10. Views of base before and after treatment (Courtesy of the Walters Art Museum)

Fig. 11. View of reassembled object after treatment (Courtesy of the Walters Art Museum)

8. CONCLUSIONS

This complex object still conceals mysteries about its manufacture and original appearance, but some conclusions were reached from this analysis and treatment. The nargile was constructed from separate pieces, each with a different silver alloy containing varying levels of silver, copper, lead, zinc, and gold. The surface color was unified with an overall gilding layer. The method of gilding can be inferred through process of elimination: no mercury detected and thus not amalgam gilt, not enough gold present in the alloy for depletion gilding or tombaga (La Niece and Craddock 1993, 188), and not a cold application of gold leaf and binder because of the surface texture and detail. Two likely options remain: electroplating or diffusion gilding (Philadelphia Museum of Art 2015). The extreme fragility of the gilded surface suggests diffusion gilding.

This treatment epitomized the theme of the conference, "making it work," because this, like many projects in the real world, presented a problem with no straightforward solution. It was a surprise to us to identify a gilding layer so thin that a soft cosmetic sponge could abrade it away. Aesthetically, we are pleased with the outcome after treatment. We were able to clean the surface without disturbing the fragile gilding while also protecting the solvent-sensitive resin carrying the dyes in the foil-backed gemstones. We feel as good as we can about our methodology, but we understand that cleaning with silver dip leaves a complex on the surface that is not well understood, and it will likely present a visual shift in the future. It is an unfavorable method in the current conservation lexicon but was the least harmful solution for this object and situation. We thought it was important to bring forward our findings and share them with the conservation community who might encounter similarly fragile gilding layers, and encourage others to investigate similar surfaces on their collections.

ACKNOWLEDGMENTS

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NOTES

1. A stylistic attribution made by Robert Mintz, Chief Curator and Curator of Asian Art at the Walters Art Museum.

2. XRF analysis was performed with a Bruker AXS Artax equipped with a rhodium tube collimated to 1.5 mm diameter at 50 kV and 200 μA for 120 seconds without a filter.

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Qosmedix
2002-Q Orville Dr. North
Ronkonkoma, NY 11779
631-242-3270
http://www.qosmedix.com/pages/product/117/20147/36-Piece-Sponge-Block-White.aspx

Cotton swabs, Solon Care 56225
Careforde
233 S. Wacker Dr.
Suite 8400
Chicago, IL 60606
800-830-4050
http://careforde.com/solon-applicators-56225-cotton-tipped-applicator-6-x-1-12-wood-stick-tapered-tip-100-bg-10-bg-bx-10-bx-cs/

Duraglit Wadding Polish, now called Silvo Wadding Polish
Conservation Support Systems
PO Box 91746
Santa Barbara, CA 93190-1746
800-482-6299
http://www.conservationsupportsystems.com/product/show/duraglit-wadding-polish/polishing-materials

Mylar polyester film roll, 2 mil.
Talas
330 Morgan Ave.
Brooklyn NY 11211
212-219-0770
http://talasonline.com

Northern Lab-Goddards 707684 Goddard's Long Shine Silver Care Cloth (17.5 in. × 13 in.); Pacific Silvercloth
Amazon
1200 12th Ave. South
Suite 1200
Seattle, WA 98144
888-280-3321
http://www.amazon.com

Precipitated calcium carbonate, CAS NO: 471-34-1, USP/NF, .04 micron
Sciencelab.com Inc.
14025 Smith Rd.
Houston, TX 77396
800-901-7247
www.sciencelab.com

Staedtler Mars plastic erasers
Office Depot
800-463-3768
http://www.officedepot.com/a/products/120451/Staedtler-Mars-Plastic-Erasers-Pack-Of/?cm_mmc=PLA-_-Bing-_-Drafting-_-120451_

Stoddard solvent; Sulfuric acid, ACS reagent
Thermo Fisher Scientific
81 Wyman St.
Waltham, MA 02451
800-766-7000
http://www.fishersci.com

Thiourea, ACS reagent
Sigma-Aldrich
3050 Spruce St.
St. Louis, MO 63103
800-325-3010
http://www.sigmaaldrich.com/catalog/product/sial/t8656?lang=en&region=US

Webril Handi-Pads, 4 in. × 4 in.
Uline
12575 Uline Dr.
Pleasant Prairie, WI 53158
800-295-5510
http://www.uline.com/Product/Detail/S-20682/Wipers/Webril-Handi-Pads?pricode=WY233&utm_source=Bing&utm_medium=pla&utm_term=S-20682&utm_campaign=Janitorial%2BSupplies

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GLENN GATES is a Conservation Scientist at the Walters Art Museum. Glenn has a PhD in physical (polymer) chemistry and a master's degree in materials science and engineering. Previously, he worked at the Detroit Institute of Arts, Harvard Art Museums, and the National Gallery of Art in Washington, DC. He has worked at the Walters since 2010.

JULIE LAUFFENBURGER is the Dorothy Wagner Wallis Director of Conservation and Technical Research at the Walters Art Museum, where she has been a staff Conservator for 25 years. In her role as Objects Conservator, Julie specializes in technical study and treatment of the art of the ancient Americas, which is supported by the endowed William B. Ziff, Jr. Conservator of Objects. Julie graduated with an MA and CAS in art conservation from Buffalo State College in 1989 and a BA in art history from Cornell University in 1985.